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(54) SPINEL MANGANESE OXIDE FOR LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve cycle characteristics.

SOLUTION: This manganese oxide is $Li_{1+x}Mn_{2-x-y}Ga_xM_yO_{4+z}$ ($0 \leq x < 0.15$, $0.01 < x < 0.2$, $0 \leq y < 0.2$ and $z \geq 0$, M is a divalent or trivalent metal), having a spinel structure, obtained by baking lithium hydroxide, chemically-synthesized manganese dioxide, gallium nitrate, and metallic nitrate at 400 to 570° C, and reheat-treating them. Part of 8a site is occupied by Ga, and the peak ((220) diffraction line) intensity of $2\theta=39^\circ$ in XRD measured by using FeK α rays is 1/4 or more of the peak ((222) diffraction line) intensity of $2\theta=48^\circ$.

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(54)【発明の名称】 リチウム二次電池用スピネル系マンガン酸化物

(57)【要約】

【目的】 この発明は、高エネルギー密度型のリチウム二次電池用正極物質として使用する8aサイトの一部をGaで置換したGaドーブリチウムリッチスピネル化合物Li_{1+x}Mn_{2-x-y}, Ga_xM_yO_{4+z} (0≤x<0.15, 0.01<x<0.2, 0≤y<0.2, z≥0: Mは2価あるいは3価の金属)を提供する。

【構成】 水酸化リチウム、化学合成二酸化マンガン、硝酸ガリウムおよび金属硝酸塩を、400-570°Cで焼成し、再度熱処理して得られるスピネル構造のLi_{1+x}Mn_{2-x-y}, Ga_xM_yO_{4+z} (0≤x<0.15, 0.01<x<0.20≤y<0.2, z≥0: Mは2価あるいは3価の金属)で、8aサイトの一部をGaが占め、Fe K_α線をもちいて測定したXRD中の2θ=39°のピーク((220)回折線)強度が2θ=48°のピーク((222)回折線)強度の1/4以上となる化合物。

1

【0001】

【特許請求の範囲】

1. 組成式 $Li_{1+x}Mn_{2-x-y}Ga_xM_yO_{4+z}$ で表せるスピネル構造を有するリチウムマンガン複酸化物 ($0 \leq x < 0.15$, $0.01 < x < 0.2$, $0 \leq y < 0.2$) で、 $FeK\alpha$ 線をもちいて測定した XRD 中の $2\theta = 39^\circ$ のピーク ((220) 回折線) 強度が $2\theta = 48^\circ$ のピーク ((222) 回折線) 強度の $1/4$ 以上となる化合物。

4. 前述の $Li_{1+x}Mn_{2-x-y}Ga_xM_yO_{4+z}$ を正極活物質とするリチウム二次電池およびカーボンなどインターカレーション化合物を負極とするロッキングチャート型リチウムイオン電池用正極。

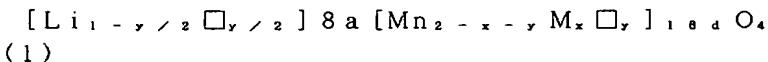
【0002】

【発明の詳細な説明】

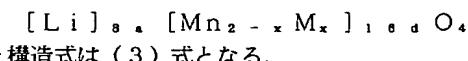
【産業上の利用分野】本発明は、金属リチウムあるいはリチウムカーボン(リチウム-グラファイト)などのインターカレーション化合物を負極活物質とするリチウム二次電池において、正極活物質として使用するスピネル構造の $Li_{1+x}Mn_{2-x-y}Ga_xM_yO_{4+z}$ 。

【0003】

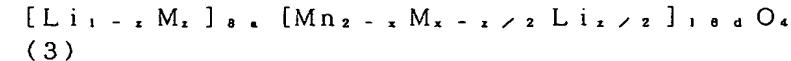
【従来の技術および問題点】4 ボルト系高エネルギー密度型のリチウム二次電池用正極活物質としては $LiNiO_2$ の他、 $LiCoO_2$ 、 $LiMn_2O_4$ が使用可能である。 $LiCoO_2$ を正極活物質とする電池は既に市販されている。しかしコバルトは資源量が少なく且つ高価であるため、電池の普及に伴う大量生産には向かない。資源量や価格の面から考えるとマンガン化合物が有望な正極材料である。原料として使用可能な二酸化マンガンは現在乾電池材料として大量に生産されている。スピネル構造の $Li_{1+x}Mn_{2-x-y}Ga_xM_yO_{4+z}$ は空格子点を $8a$ 、および $16d$ はスピネル構造中のサイトを示す。 y の値は合成条件に依存するが、適切な合成条件を選べば $y = 0$ となる。この無欠陥の金



ここで \square は空格子点を $8a$ 、および $16d$ はスピネル構造中のサイトを示す。 y の値は合成条件に依存するが、適切な合成条件を選べば $y = 0$ となる。この無欠陥の金



の一部が置換されると構造式は (3) 式となる。



上式から分かるように $16d$ サイトは Li , Mn , M と 3 種の元素からなり、サイクル特性の優れた異種金属置換リチウムリッチスピネルと同一の元素構成となる。また、充電に伴う脱リチウムに際して $8a$ サイトに金属が残存するため $-MnO_2$ の生成が阻害され、サイクル特性の向上が期待できる。以上サイクル特性が向上する要因に加えて、 $8a$ サイトに M が置換する結果リチウムと金属の比が 0.5 の組成でもリチウムリッチタイプの $16d$ サイトの構成となり、リチウムの原子比を 0.5 以上にする必要はなく、リチウムリッチにする事による容量低下を避けることができる。従来 $8a$ サイトに置換

* ル構造の $LiMn_2O_4$ はサイクルを重ねると容量が低下する欠点があり、この欠点を改善するために Mg や Zn 等の添加 (Thackeray ら, Solid State Ionics, 69, 59 (1994)) や Co , Ni , Cr 等の添加 (岡田ら、電池技術, Vol. 5, (1993)) が行われ、その有効性が既に明らかにされている。しかしながら $50^\circ C$ 以上の高温作動時には電解液への Mn 溶解が顕著となるため、サイクルに伴う容量低下が大きく単純に上述の金属をドープしただけでは正極の十分なサイクル寿命を保持することは困難である。

【0004】

【発明が解決しようとする課題】本発明は、かかる従来技術の課題に鑑みなされたもので、従来の $16d$ サイトの Mn を異種金属元素で置換するのではなく、 $8a$ サイトの Li を異種金属元素で置換し、従来とは異なった $8a$ サイト金属置換型のマンガンスピネル化合物を使用することによりサイクル特性の向上を目指すものである。

【0005】

【問題点を解決するための手段】通常異種金属を添加してスピネルリチウムマンガン化合物を合成すると $16d$ サイトの Mn の位置に異種金属元素が置換したスピネル構造の化合物が生成する。典型元素の Mg や 4 配位を取りやすい Zn で置換した場合でも $16d$ サイトの置換が起こり、XRD 図には顕著な変化はみられない。リチウムと金属 ($Mn + M$) の原子比 ($Li / (Mn + M)$) が 0.5 の金属置換マンガンのスピネル構造式は一般に (1) 式で表される (芳尾ら、電気化学, 66, 335 (1998))。

20

※ 属置換スピネルマンガン化合物の構造式は (2) 式で表される。ここで $8a$ サイトに M

40 される金属は知られていなかったが我々は Ga が $8a$ サイトに置換されることを発見した。 $8a$ サイトへの置換は XRD 測定により確認できる。 Ga ドープのスピネル化合物 ($LiMn_{1.8}Ga_{0.1}O_4$) と $LiMn_2O_4$ の $FeK\alpha$ 線を用いて測定した XRD 図を図 1 に示す。 $LiMn_{1.8}Ga_{0.1}O_4$ のピークパターンは $LiMn_2O_4$ と同じであり、スピネル構造であることが確認できる。また、不純物に起因するピークも認められない。大きな違いは $2\theta = 39^\circ$ のピーク ((220) 回折線) 強度が增加することと $2\theta = 71^\circ$ に弱いピークが出現することである。この $2\theta = 71^\circ$ ピーク

は(422)回折線であることを確認した。リートベルト法を用いて $\text{LiMn}_{1.8} \text{Ga}_{0.1} \text{O}_4$ の8aサイトを占めるGaの割合を求めたところ約4%のGaが8aサイトを占めていることが分かった。即ち、Gaは8aサイトと16dサイトの両方に分布することが分かった。Gaドープ量を増すと8aサイトのGa占有率が増し、(220)回折線の強度(I_{220})が増す一方、(222)回折線の強度(I_{222})が減少する。約4%のGaが8aサイトを占める場合、 I_{220}/I_{222} の値は約0.5であるがGaの8aサイト占有率が15%まで増加するとこの値は約2まで増加する。即ち、この強度比はGaの8aサイト占有率を示すパラメータとして使用できる。8aサイトを異種金属で置換すると上述したようにサイクル特性の改善が期待できる。実際にサイクル特性改善できるか調べてみた。測定は容量低下が大きい50°Cで行った。実施例2で製造した $\text{LiMn}_{1.85} \text{Ga}_{0.05} \text{O}_4$ を正極活物質とし、リチウム二次電池特性を調べた。電解液は1M LiPF₆-EC·DMC(体積比1:2)である。第1回目の放電容量は130mA/gであり、50サイクル目でも123mA/h/gの容量を示しサイクル特性が優れていることが確認できた。

【0006】GaとともにCo, Cr, Ni, Fe, Zn, Mgを加えても I_{220}/I_{222} の強度比に大きな違いは見られず、 $\text{LiMn}_{2-x} \text{Ga}_x \text{M}_y \text{O}_4$ で表されるスピネル化合物でもGaが8aサイトを占めることが確認できた。またこれらの化合物のサイクル特性は良好で50サイクル後の容量保持率(50サイクル目の容量/1サイクル目の容量)は95%以上であった。

【0007】

【発明の効果】本法で製造した8aサイト異種金属置換のスピネルマンガン酸化物はリチウム二次電池正極としての機能を有し、高温でのサイクル特性がすぐれるため、高温環境で使用されるリチウムイオン電池あるいはリチウム二次電池の正極活物質として有用である。

【0008】

【実施例】

【実施例1】水酸化リチウム、化学合成二酸化マンガン、硝酸ガリウムを1:1.90:0.10のモル比で混合粉碎する。470°Cで5時間加熱後、更に530°Cで5時間加熱した。冷却後、粉碎し更に700°Cで20時間焼成した。この試料はリートベルト解析により $[\text{Li}_{1.857} \text{Ga}_{0.043}]_{8a} [\text{Li}_{0.022} \text{Mn}_{1.900} \text{Ga}_{0.078}]_{16d} \text{O}_4$ のスピネル構造式表せる化合物であることが確認できた。

【0009】

【実施例2】水酸化リチウム、化学合成二酸化マンガン、硝酸ガリウムを1:1.95:0.05のモル比で混合粉碎する。470°Cで5時間加熱後、更に530°C

で5時間加熱した。冷却後、粉碎し更に700°Cで20時間焼成した。この試料の I_{220}/I_{222} は0.4であり、8aサイトをGaが占有することが確認できた。上記試料25mgと導電性バインダー10mgを用いてフィルム状合剤を作成し、ステンレスメッシュに圧着して正極とした。正極は200°Cで乾燥して使用した。負極には金属リチウムを、電解液にはLiBF₄-EC·DMC(体積比1:2)を用いた。充放電電流は0.25mA(0.1mA/cm²)とし、充放電電圧範囲は4.5-3.5Vとした。充放電テストは50°Cで行った。以下の実施例、比較例での評価は全て上記の条件で行った。

【0010】

【実施例3】水酸化リチウム、化学合成二酸化マンガン、硝酸ガリウム、硝酸コバルトを1:1.90:0.05:0.05のモル比で混合粉碎する。470°Cで5時間加熱後、更に530°Cで5時間加熱した。冷却後、粉碎し更に750°Cで20時間焼成した。この試料の I_{220}/I_{222} は0.4であり、8aサイトをGaが占有することが確認できた。この試料の第1回目の放電容量は125mA/h/g以上であり50サイクル目の容量保持率も95%以上であった。

【実施例4】水酸化リチウム、化学合成二酸化マンガン、硝酸ガリウム、硝酸ニッケルを1:1.90:0.05:0.05のモル比で混合粉碎する。470°Cで5時間加熱後、更に530°Cで5時間加熱した。冷却後、粉碎し更に750°Cで20時間焼成した。この試料の I_{220}/I_{222} は0.4であり、8aサイトをGaが占有することが確認できた。この試料の第1回目の放電容量は118mA/h/g以上であり50サイクル目の容量保持率も95%以上であった。

【実施例5】水酸化リチウム、化学合成二酸化マンガン、硝酸ガリウム、硝酸クロムを1:1.90:0.05:0.05のモル比で混合粉碎する。470°Cで5時間加熱後、更に530°Cで5時間加熱した。冷却後、粉碎し更に750°Cで20時間焼成した。この試料の I_{220}/I_{222} は0.4であり、8aサイトをGaが占有することが確認できた。この試料の第1回目の放電容量は125mA/h/g以上であり50サイクル目の容量保持率も95%以上であった。

【0011】

【実施例6】水酸化リチウム、化学合成二酸化マンガン、硝酸ガリウム、酸化第二鉄を1:1.90:0.05:0.05のモル比で混合粉碎する。470°Cで5時間加熱後、更に530°Cで5時間加熱した。冷却後、粉碎し更に750°Cで20時間焼成した。この試料の I_{220}/I_{222} は0.45であり、8aサイトをGaが占有することが確認できた。この試料の第1回目の放電容量は120mA/h/g以上であり50サイクル目の容量保持率も95%以上であった。

【実施例7】水酸化リチウム、化学合成二酸化マンガン、硝酸ガリウム、硝酸亜鉛を1:1.90:0.05:0.05のモル比で混合粉碎する。470°Cで5時間加熱後、更に530°Cで5時間加熱した。冷却後、粉碎し更に750°Cで20時間焼成した。この試料の I_{220}/I_{222} は0.4であり、8aサイトをGaが占有することが確認できた。この試料の第1回目の放電容量は118mA·h/g以上であり50サイクル目の容量保持率も95%以上であった。

【実施例8】水酸化リチウム、化学合成二酸化マンガン、硝酸ガリウム、硝酸マグネシウムを1:1.90:0.05:0.05のモル比で混合粉碎する。470°Cで5時間加熱後、更に530°Cで5時間加熱した。冷却後、粉碎し更に750°Cで20時間焼成した。この試料の I_{220}/I_{222} は0.3であり、8aサイトをGaが占有することが確認できた。この試料の第1回目の*

*放電容量は118mA·h/g以上であり50サイクル目の容量保持率も95%以上であった。

【0011】

【比較例1】水酸化リチウム、化学合成二酸化マンガンを1:2のモル比で混合粉碎する。470°Cで5時間加熱後、更に530°Cで5時間加熱した。冷却後、粉碎し更に700°Cで20時間焼成した。この試料の I_{220}/I_{222} は0.22であった。同一条件で数回実験を繰り返した結果この値は0.20-0.28の範囲であった。

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【図面の簡単な説明】

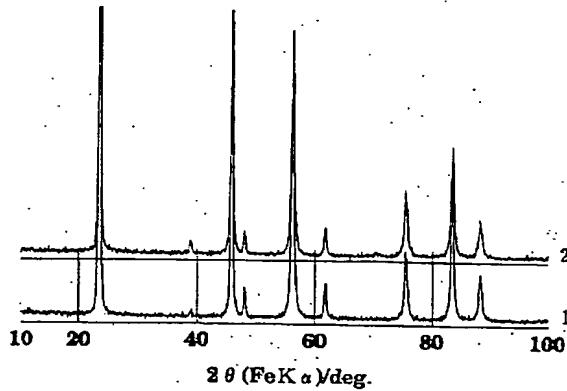
【図1】 LiMn_2O_4 と $\text{LiMn}_{1.8}\text{Ga}_{0.2}\text{O}_4$ のX線回折図

【符号の説明】

1: LiMn_2O_4

2: $\text{LiMn}_{1.8}\text{Ga}_{0.2}\text{O}_4$

【図1】



JAPANESE

[JP,2000-058058,A]

AJ

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD EFFECT OF THE INVENTION TECHNICAL
PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

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CLAIMS

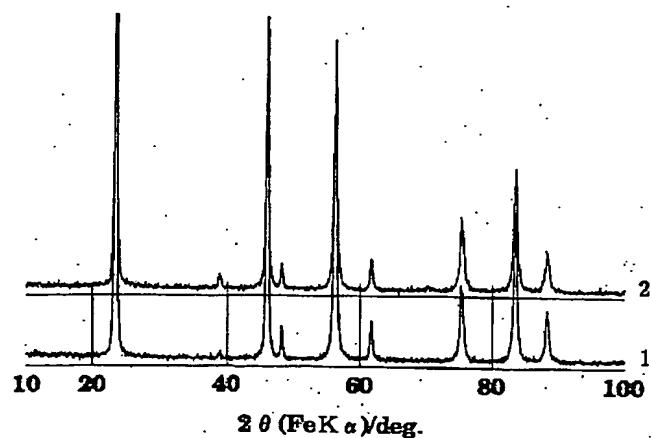
[0001]

[Claim(s)]

1. By Lithium Manganese Multiple Oxide ($0 \leq X \leq 0.15$, $0.01 < X < 0.2$, $0 \leq Y \leq 0.2$) Which Has Spinel Structure Which Can be Expressed with Empirical-Formula $Li_1+XMn_2-X-yGaxMyO_4+Z$ The compound with which it is with FeK alpha rays, and the $2\theta=39$ degree peak (220) (diffraction line) intensity in measured XRD becomes 1/4 or more [of the peak (222) (diffraction line) intensity which is $2\theta=48$ degree].
4. Positive electrode for rocking-chair type lithium ion batteries which uses as negative electrode intercalation compounds, such as lithium secondary battery, carbon, etc. which make above-mentioned $Li_1+xMn_2-x-yGaxMyO_4+z$ positive active material.

[0002]

[Translation done.]

Drawing selection drawing 1 

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application] this invention is $Li_{1+x}Mn_{2-x-y}Ga_xM_yO_{4+z}$ of the Spinel structure which uses intercalation compounds, such as a metal lithium or lithium carbon (lithium-graphite), as a positive active material in the lithium secondary battery made into a negative-electrode active material.

[Description of the Prior Art] As a 4-volt system high-energy density type positive active material for lithium secondary batteries, $LiCoO_2$ besides $LiNiO_2$ and $LiMn_2O_4$ are usable. The cell which makes $LiCoO_2$ a positive active material is already marketed. However, since there are few amounts of resources and cobalt's are expensive, it is not fit for mass production method accompanying the spread of cells. When it thinks from the field of the amount of resources, or a price, a manganese compound is a promising positive-electrode material. Manganese dioxide usable as a raw material is produced in large quantities as a dry cell material now. $LiMn_2O_4$ of Spinel structure has the fault to which capacity falls, when a cycle is piled up, in order to improve this fault, addition (Okada et al., cell technology, Vol.5, (1993)) which is addition (69 Thackeray et al., Solid State Ionics, 59 (1994)) of Mg, Zn, etc., Co, nickel, Cr, etc. is performed, and the effectiveness is already clarified. However, since Mn dissolving in the electrolytic solution becomes remarkable at the time of the elevated-temperature operation of 50 degrees C or more, it is difficult to hold sufficient cycle life of a positive electrode only by the capacity fall accompanying a cycle doping an above-mentioned metal simply greatly.

[0004]

[Problem(s) to be Solved by the Invention] this invention was not made in view of the technical problem of this conventional technology, and does not replace Mn of the conventional 16d site by the dissimilar-metal element, but replaces Li of 8a site by the dissimilar-metal element, and aims at improvement in a cycle property by using a different 8a site metal-replacement type manganese spinel compound from the former -- it is a thing

[0005]

[Means for Solving the Problem] Usually, if a dissimilar metal is added and a spinel lithium manganese compound is compounded, the compound of the Spinel structure which the dissimilar-metal element replaced by the position of Mn of 16d site will generate. Even when it replaces by Zn which is easy to take Mg of a typical element, and 4 coordination, the substitution of 16d site takes place, and a change remarkable in a XRD view is not seen. Generally as for the Spinel structure formula of the metal-replacement manganese of 0.5, the atomic ratio ($Li/(Mn+M)$) of a lithium and a metal ($Mn+M$) is expressed with (1) formula (Yoshio et al., electrochemistry, 66,335 (1998)).

[2**y $[Li_{1-y}/2]8a[Mn_{2-x-y}M_x^{**y}]16dO_4$ (1)]

A vacancy is shown by ** and the site in Spinel structure is shown 8a and 16d here. Although it is dependent on synthetic conditions, the value of y will be set to y= 0 if suitable synthetic conditions are chosen. The structure expression of this defect-free metal-replacement spinel manganese compound is expressed with (2) formulas. It is here and is M to 8a site. (2) $[Li]8a[Mn_{2-x}M_x]16dO_4$

If ***** is replaced, a structure expression will turn into (3) formulas.

[$Li_{1-z}M_z$]8a $[Mn_{2-x}M_x-z/2Li_z]16dO_4$ (3)

As shown in an upper formula, 16d site consists of Li, Mn, M, and three sorts of elements, and serves as the same element composition as the dissimilar-metal substitution lithium rich spinel which was excellent in the cycle property. Moreover, since a metal remains to 8a site on the occasion of the ** lithium accompanying charge, generation of $\lambda-MnO_2$ is checked, and improvement in a cycle property can be expected. the factor whose cycle property improves above -- in addition, the result which M replaces by 8a site -- the ratio of a lithium and a metal -- composition of 0.5 -- the composition of lithium rich type 16d site -- becoming -- the atomic ratio of a lithium -- 0.5 or more -- it is not necessary to carry out -- a lithium -- the capacity fall by making it rich is avoidable. Although the metal conventionally replaced by 8a site was not known, we discovered that Ga was replaced by 8a site. The substitution to 8a site can be checked by XRD measurement. The spinel compound ($LiMn_{1.9}Ga_{0.1}O_4$) of Ga dope and the XRD view measured using the FeK alpha rays of $LiMn_2O_4$ are shown in drawing 1. The peak pattern of $LiMn_{1.9}Ga_{0.1}O_4$ is the same as $LiMn_2O_4$, and it can check that it is Spinel structure. Moreover, the

peak resulting from an impurity is not accepted, either. A big difference is that 2theta=39 degree peak (220) (diffraction line's) intensity's increasing and a peak weak at 2theta=71 degree appear. It checked that this 2 theta=71-degree peak was a diffraction (422) line. When the rate of Ga which occupies 8a site of LiMn1.9Ga 0.1O4 using the lied belt method was searched for, it turns out that about 4% of Ga occupies 8a site. That is, it turns out that Ga is distributed over both 8a site and 16d site. If the amount of Ga dopes is increased, while the intensity (I220) of the increase of Ga pulse duty factor of 8a site and a diffraction (220) line will increase, the intensity (I222) of a diffraction (222) line decreases. the case where about 4% of Ga occupies 8a site -- the value of I220/I222 -- about -- although it comes out 0.5, if 8a site pulse duty factor of Ga increases to 15%, this value will increase to about 2. That is, this intensity ratio can be used as a parameter which shows 8a site pulse duty factor of Ga. When 8a site was replaced by the dissimilar metal, as it mentioned above, an improvement of a cycle property is expectable. It investigated whether a cycle property improvement could actually be carried out. The capacity fall performed measurement at large 50 degrees C. LiMn1.95G0.05O4 manufactured in the example 2 were made into the positive active material, and the lithium secondary battery property was investigated. The electrolytic solution is 1M. It is LiPF6-EC-DMC (volume ratio 1:1). The 1st service capacity is 130 mA/g and it has checked that the capacity of 123 mA/g was shown and the cycle property was excellent also in 50 cycle eye.

[0006] Even if it added Co, Cr, nickel, Fe, Zn, and Mg with Ga, the big difference to the intensity ratio of I220/I222 was not seen, but the spinel compound expressed with LiMn_{2-x-y}Ga_xMyO₄ has also checked that Ga occupied 8a site. Moreover, the cycle property of these compounds was good and the capacity retention after 50 cycles (capacity of the capacity / 1 cycle eye of 50 cycle eye) was 95% or more.

[0007]

[Effect of the Invention] Since it has a function as a lithium secondary battery positive electrode and the cycle property in an elevated temperature is excellent, the spinel manganic acid ghost of 8a site dissimilar-metal substitution manufactured by this method is useful as a positive active material of the lithium ion battery used by hot environments, or a lithium secondary battery.

[0008]

[Example]

[Example 1] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, and the nitric-acid gallium is carried out by the mole ratio of 1:1.90:0.10. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 700 more degrees C for 20 hours. This sample has checked that it was the Spinel structure formula table **** compound of [Li0.957Ga0.043]8a [Li0.022Mn1.900Ga0.078]16dO4 in lied belt analysis.

[0009]

[Example 2] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, and the nitric-acid gallium is carried out by the mole ratio of 1:1.95:0.05. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 700 more degrees C for 20 hours. I220/I222 of this sample are 0.4, and it has checked that Ga occupied 8a site. the 25mg of the above-mentioned samples, and conductive binder 10mg -- using -- the shape of a film -- the mixture was created, and it was stuck to a stainless steel mesh by pressure, and considered as the positive electrode. The positive electrode was dried and used at 200 degrees C. The metal lithium was used for the negative electrode and LiBF4-EC-DMC (volume ratio 1:2) was used for the electrolytic solution. The charge and discharge current was set to 0.25mA (0.1 mA/cm²), and the charge-and-discharge-voltage range was set to 4.5-3.5V. The charge-and-discharge test was performed at 50 degrees C. All evaluations in the following examples and the example of comparison were performed on condition that the above.

[0010]

[Example 3] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, a nitric-acid gallium, and the cobalt nitrate is carried out by the mole ratio of 1:1.90:0.05:0.05. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 750 more degrees C for 20 hours. I220/I222 of this sample are 0.4, and it has checked that Ga occupied 8a site. The 1st service capacity of this sample was 125 or more mA/g, and the capacity retention of 50 cycle eye was also 95% or more.

[Example 4] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, a nitric-acid gallium, and the nickel nitrate is carried out by the mole ratio of 1:1.90:0.05:0.05. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 750 more degrees C for 20 hours. I220/I222 of this sample are 0.4, and it has checked that Ga occupied 8a site. The 1st service capacity of this sample was 118 or more mA/g, and the capacity retention of 50 cycle eye was also 95% or more.

[Example 5] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, a nitric-acid gallium, and the chromium nitrate is carried out by the mole ratio of 1:1.90:0.05:0.05. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 750 more degrees C for 20 hours. I220/I222 of this sample are 0.4, and it has checked that Ga occupied 8a site. The 1st service capacity of this sample was 125 or more mA/g, and the capacity retention of 50 cycle eye was also 95% or more.

[0011]

[Example 6] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, a nitric-acid gallium, and the ferric oxide is carried out by the mole ratio of 1:1.90:0.05:0.05. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 750 more degrees C for 20 hours. I220/I₂22 of this sample are 0.45 and it has checked that Ga occupied 8a site. The 1st service capacity of this sample was 120 or more mAh/g, and the capacity retention of 50 cycle eye was also 95% or more.

[Example 7] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, a nitric-acid gallium, and the zinc nitrate is carried out by the mole ratio of 1:1.90:0.05:0.05. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 750 more degrees C for 20 hours. I220/I₂22 of this sample are 0.4, and it has checked that Ga occupied 8a site. The 1st service capacity of this sample was 118 or more mAh/g, and the capacity retention of 50 cycle eye was also 95% or more.

[Example 8] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, a nitric-acid gallium, and the magnesium nitrate is carried out by the mole ratio of 1:1.90:0.05:0.05. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 750 more degrees C for 20 hours. I220/I₂22 of this sample are 0.3, and it has checked that Ga occupied 8a site. The 1st service capacity of this sample was 118 or more mAh/g, and the capacity retention of 50 cycle eye was also 95% or more.

[0011]

[The example 1 of comparison] Preferential grinding of a lithium hydroxide and chemosynthesis manganese dioxide is carried out by the mole ratio of 1:2. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 700 more degrees C for 20 hours. I220/I₂22 of this sample were 0.22. As a result of repeating an experiment several times on the same conditions, the range of this value was 0.20-0.28.

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TECHNICAL FIELD

[Industrial Application] this invention is $Li_{1+x}Mn_{2-x-y}Ga_xMyO_{4+z}$ of the Spinel structure which uses intercalation compounds, such as a metal lithium or lithium carbon (lithium-graphite), as a positive active material in the lithium secondary battery made into a negative-electrode active material.

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EFFECT OF THE INVENTION

[Effect of the Invention] Since it has a function as a lithium secondary battery positive electrode and the cycle property in an elevated temperature is excellent, the spinel manganic acid ghost of 8a site dissimilar-metal substitution manufactured by this method is useful as a positive active material of the lithium ion battery used by hot environments, or a lithium secondary battery.

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TECHNICAL PROBLEM

[Description of the Prior Art] As a 4v system high-energy density type positive active material for lithium secondary batteries, LiCoO₂ besides LiNiO₂ and LiMn₂O₄ are usable. The cell which makes LiCoO₂ a positive active material is already marketed. However, since there are few amounts of resources and cobalt's are expensive, it is not fit for mass production method accompanying the spread of cells. When it thinks from the field of the amount of resources, or a price, a manganese compound is a promising positive-electrode material. Manganese dioxide usable as a raw material is produced in large quantities as a dry cell material now. LiMn₂O₄ of Spinel structure has the fault to which capacity falls, when a cycle is piled up, in order to improve this fault, addition (Okada et al., cell technology, Vol.5, (1993)) which is addition (69 Thackeray et al., Solid State Ionics, 59 (1994)) of Mg, Zn, etc., Co, nickel, Cr, etc. is performed, and the effectiveness is already clarified. However, since Mn dissolving in the electrolytic solution becomes remarkable at the time of the elevated-temperature operation of 50 degrees C or more, it is difficult to hold sufficient cycle life of a positive electrode only by the capacity fall accompanying a cycle doping an above-mentioned metal simply greatly.

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MEANS

[Means for Solving the Problem] Usually, if a dissimilar metal is added and a spinel lithium manganese compound is compounded, the compound of the Spinel structure which the dissimilar-metal element replaced by the position of Mn of 16d site will generate. Even when it replaces by Zn which is easy to take Mg of a typical element, and 4 coordination, the substitution of 16d site takes place, and a change remarkable in a XRD view is not seen. Generally as for the Spinel structure formula of the metal-replacement manganese of 0.5, the atomic ratio (Li/(Mn+M)) of a lithium and a metal (Mn+M) is expressed with (1) formula (Yoshio et al., electrochemistry, 66,335 (1998)).

[$2^{**}y [Li1-y]/2]8a[Mn2-x-yMx^{**}y] 16dO4$ (1)

A vacancy is shown by ** and the site in Spinel structure is shown 8a and 16d here. Although it is dependent on synthetic conditions, the value of y will be set to y= 0 if suitable synthetic conditions are chosen. The structure expression of this defect-free metal-replacement spinel manganese compound is expressed with (2) formulas. It is here and is M to 8a site. (2) $[Li]8a[Mn2-xMx]16dO4$

If ***** is replaced, a structure expression will turn into (3) formulas.

$[Li1-zMz]8a[Mn2-xMx-z/2Liz/2]16dO4$ (3)

As shown in an upper formula, 16d site consists of Li, Mn, M, and three sorts of elements, and serves as the same element composition as the dissimilar-metal substitution lithium rich spinel which was excellent in the cycle property. Moreover, since a metal remains to 8a site on the occasion of the ** lithium accompanying charge, generation of lambda-MnO₂ is checked, and improvement in a cycle property can be expected. the factor whose cycle property improves above -- in addition, the result which M replaces by 8a site -- the ratio of a lithium and a metal -- composition of 0.5 -- the composition of lithium rich type 16d site -- becoming -- the atomic ratio of a lithium -- 0.5 or more -- it is not necessary to carry out -- a lithium -- the capacity fall by making it rich is avoidable. Although the metal conventionally replaced by 8a site was not known, we discovered that Ga was replaced by 8a site. The substitution to 8a site can be checked by XRD measurement. The spinel compound (LiMn_{1.9}Ga_{0.1}O₄) of Ga dope and the XRD view measured using the FeK alpha rays of LiMn₂O₄ are shown in drawing 1. The peak pattern of LiMn_{1.9}Ga_{0.1}O₄ is the same as LiMn₂O₄, and it can check that it is Spinel structure. Moreover, the peak resulting from an impurity is not accepted, either. A big difference is that 2theta=39 degree peak (220) (diffraction line's) intensity's increasing and a peak weak at 2theta=71 degree appear. It checked that this 2 theta=71-degree peak was a diffraction (422) line. When the rate of Ga which occupies 8a site of LiMn_{1.9}Ga_{0.1}O₄ using the lied belt method was searched for, it turns out that about 4% of Ga occupies 8a site. That is, it turns out that Ga is distributed over both 8a site and 16d site. If the amount of Ga dopes is increased, while the intensity (I₂₂₀) of the increase of Ga pulse duty factor of 8a site and a diffraction (220) line will increase, the intensity (I₂₂₂) of a diffraction (222) line decreases. the case where about 4% of Ga occupies 8a site -- the value of I₂₂₀/I₂₂₂ -- about -- although it comes out 0.5, if 8a site pulse duty factor of Ga increases to 15%, this value will increase to about 2. That is, this intensity ratio can be used as a parameter which shows 8a site pulse duty factor of Ga. When 8a site was replaced by the dissimilar metal, as it mentioned above, an improvement of a cycle property is expectable. It investigated whether a cycle property improvement could actually be carried out. The capacity fall performed measurement at large 50 degrees C. LiMn_{1.95}G_{0.05}O₄ manufactured in the example 2 were made into the positive active material, and the lithium secondary battery property was investigated. The electrolytic solution is 1M. It is LiPF₆-EC-DMC (volume ratio 1:1). The 1st service capacity is 130 mA/g and it has checked that the capacity of 123 mAh/g was shown and the cycle property was excellent also in 50 cycle eye.

[0006] Even if it added Co, Cr, nickel, Fe, Zn, and Mg with Ga, the big difference to the intensity ratio of I₂₂₀/I₂₂₂ was not seen, but the spinel compound expressed with LiMn_{2-x-y}GaxMyO₄ has also checked that Ga occupied 8a site. Moreover, the cycle property of these compounds was good and the capacity retention after 50 cycles (capacity of the capacity / 1 cycle eye of 50 cycle eye) was 95% or more.

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EXAMPLE

[Example]

[Example 1] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, and the nitric-acid gallium is carried out by the mole ratio of 1:1.90:0.10. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 700 more degrees C for 20 hours. This sample has checked that it was the Spinel structure formula table **** compound of $[Li0.957Ga0.043]8a$ $[Li0.022Mn1.900Ga0.078]16dO4$ in lied belt analysis.

[0009]

[Example 2] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, and the nitric-acid gallium is carried out by the mole ratio of 1:1.95:0.05. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 700 more degrees C for 20 hours. I220/I222 of this sample are 0.4, and it has checked that Ga occupied 8a site. the 25mg of the above-mentioned samples, and conductive binder 10mg -- using -- the shape of a film -- the mixture was created, and it was stuck to a stainless steel mesh by pressure, and considered as the positive electrode. The positive electrode was dried and used at 200 degrees C. The metal lithium was used for the negative electrode and LiBF4-EC-DMC (volume ratio 1:2) was used for the electrolytic solution. The charge and discharge current was set to 0.25mA (0.1 mA/cm²), and the charge-and-discharge-voltage range was set to 4.5-3.5V. The charge-and-discharge test was performed at 50 degrees C. All evaluations in the following examples and the example of comparison were performed on condition that the above.

[0010]

[Example 3] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, a nitric-acid gallium, and the cobalt nitrate is carried out by the mole ratio of 1:1.90:0.05:0.05. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 750 more degrees C for 20 hours. I220/I222 of this sample are 0.4, and it has checked that Ga occupied 8a site. The 1st service capacity of this sample was 125 or more mAh/g, and the capacity retention of 50 cycle eye was also 95% or more.

[Example 4] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, a nitric-acid gallium, and the nickel nitrate is carried out by the mole ratio of 1:1.90:0.05:0.05. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 750 more degrees C for 20 hours. I220/I222 of this sample are 0.4, and it has checked that Ga occupied 8a site. The 1st service capacity of this sample was 118 or more mAh/g, and the capacity retention of 50 cycle eye was also 95% or more.

[Example 5] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, a nitric-acid gallium, and the chromium nitrate is carried out by the mole ratio of 1:1.90:0.05:0.05. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 750 more degrees C for 20 hours. I220/I222 of this sample are 0.4, and it has checked that Ga occupied 8a site. The 1st service capacity of this sample was 125 or more mAh/g, and the capacity retention of 50 cycle eye was also 95% or more.

[0011]

[Example 6] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, a nitric-acid gallium, and the ferric oxide is carried out by the mole ratio of 1:1.90:0.05:0.05. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 750 more degrees C for 20 hours. I220/I222 of this sample are 0.45, and it has checked that Ga occupied 8a site. The 1st service capacity of this sample was 120 or more mAh/g, and the capacity retention of 50 cycle eye was also 95% or more.

[Example 7] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, a nitric-acid gallium, and the zinc nitrate is carried out by the mole ratio of 1:1.90:0.05:0.05. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 750 more degrees C for 20 hours. I220/I222 of this sample are 0.4, and it has checked that Ga occupied 8a site. The 1st service capacity of this sample was 118 or more mAh/g, and the capacity retention of 50 cycle eye was also 95% or more.

[Example 8] Preferential grinding of a lithium hydroxide, chemosynthesis manganese dioxide, a nitric-acid gallium, and the magnesium nitrate is carried out by the mole ratio of 1:1.90:0.05:0.05. It heated at 530 more degrees C after

5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 750 more degrees C for 20 hours. I220/I222 of this sample are 0.3, and it has checked that Ga occupied 8a site. The 1st service capacity of this sample was 118 or more mAh/g, and the capacity retention of 50 cycle eye was also 95% or more.

[0011]

[The example 1 of comparison] Preferential grinding of a lithium hydroxide and chemosynthesis manganese dioxide is carried out by the mole ratio of 1:2. It heated at 530 more degrees C after 5-hour heating by 470 degrees C for 5 hours. After cooling, it ground and calcinated at 700 more degrees C for 20 hours. I220/I222 of this sample were 0.22. As a result of repeating an experiment several times on the same conditions, the range of this value was 0.20-0.28.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The X diffraction view of LiMn 2O4 and LiMn1.9Ga 0.1O4

[Description of Notations]

1:LiMn2O4

2:LiMn1.9Ga0.1O4

[Translation done.]

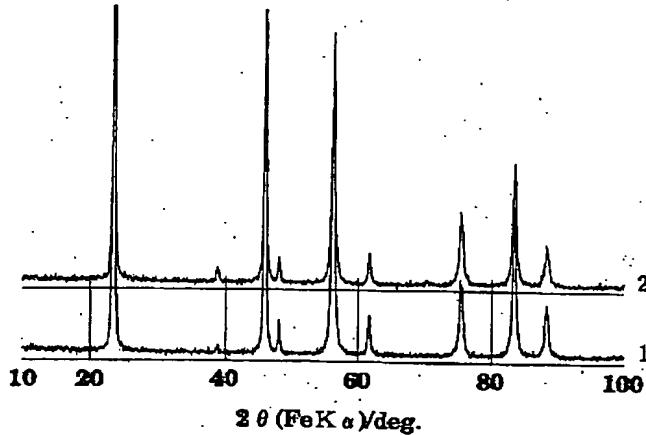
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DRAWINGS

[Drawing 1]



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